

Figure 1 | Effect of nanotwins on the mechanical properties of copper structures. **a**, Multicrystalline copper with parallel twins in each grain. **b–d**, Stress–strain curves, failure modes (left inset) and microstructures (right inset) of single-crystalline nanopillars containing only nanotwins. **b**, A 70-nm-diameter nanopillar containing parallel orthogonal twins with a spacing of 0.6 nm shows a tensile strength σ_{TS} of 2.4 GPa and ductile necking failure. **c**, A 100-nm-diameter nanopillar containing parallel orthogonal twins with a spacing of 4.3 nm shows a σ_{TS} of 2.1 GPa and brittle failure. **d**, A 50-nm-diameter nanopillar containing 18° tilted twins with a spacing of 1.2 nm shows a much lower σ_{TS} of 0.95 GPa and ductile necking failure.

brittle-to-ductile failure mode transition as the nanotwin boundary distance decreases. Remarkably, nanopillars with a diameter of 70 nm and a twin spacing of 0.6 nm exhibit both ductile necking failure and a tensile strength of 2.4 GPa, a value that is higher than that measured for nanopillars failing in a brittle manner⁵. In the case of tilted twin boundaries at 1.2 nm spacing, the nanopillars also exhibited a ductile necking failure, but at much lower strength compared with their orthogonal counterparts (Fig. 1d).

These observations were rationalized by molecular dynamic simulations: in the

case of the orthogonal twins at a spacing of 2.8 nm or less, the plastic deformation is carried out through the classical mechanism of necking and shear banding; in the case of the brittle failure observed in twins with a 4.3-nm spacing, a crack is initiated at the twin-surface junction and propagates through twin plane cleavage; and for the case of the ductile failure observed in the slanted twins, the plastic deformation is accommodated by the migration of the twin boundaries mediated by dislocation motion (a mechanism called de-twinning).

The ingenious specimen fabrication, experimental work and theoretical analysis revealed a host of different deformation mechanisms and failure patterns in nanotwinned copper nanopillars. In particular, the change of the dominant deformation mechanism from de-twinning to twin–dislocation interactions and the observation of the brittle-to-ductile failure transition provide important clues that high ductile materials with high tensile strength can be achieved by controlling nanotwin spacing and orientation.

However, despite the significant progress made in understanding the role of twins in the deformation and failure mechanisms of these nanoscale systems, it is unlikely that metallic materials based on nanotwins will soon form the basis for future materials and engineering structures. This is because the strong anisotropy associated with such nanotwin structures greatly restricts their applicability. Although nanotwins provide strong resistance to dislocation propagation (at least at a certain spacing), they can do little if dislocations run parallel to the twin boundaries, as evidenced by the work of Jang and co-workers⁵. Perhaps combining nanotwins with other strengthening mechanisms could be a fruitful avenue for future research into this fascinating class of materials towards applications, for instance, in micro- and nanoelectromechanical systems. □

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Published online: 15 July 2012

WATER DESALINATION

Graphene cleans up water

Graphene promises water desalination at throughputs much higher than state-of-the-art membranes.

Evelyn N. Wang and Rohit Karnik

Rapid population growth, industrialization and urbanization have made clean water an increasingly scarce resource, and water desalination represents one promising solution¹. Reverse

osmosis accounts for nearly half of the world's installed desalination capacity, and works by driving salt (feed) water across a semi-permeable membrane under high pressure. The membrane allows water

molecules to pass through, but not salt ions. Reverse osmosis is more energy efficient than other desalination technologies, and has been in industrial development for several decades, but struggles with

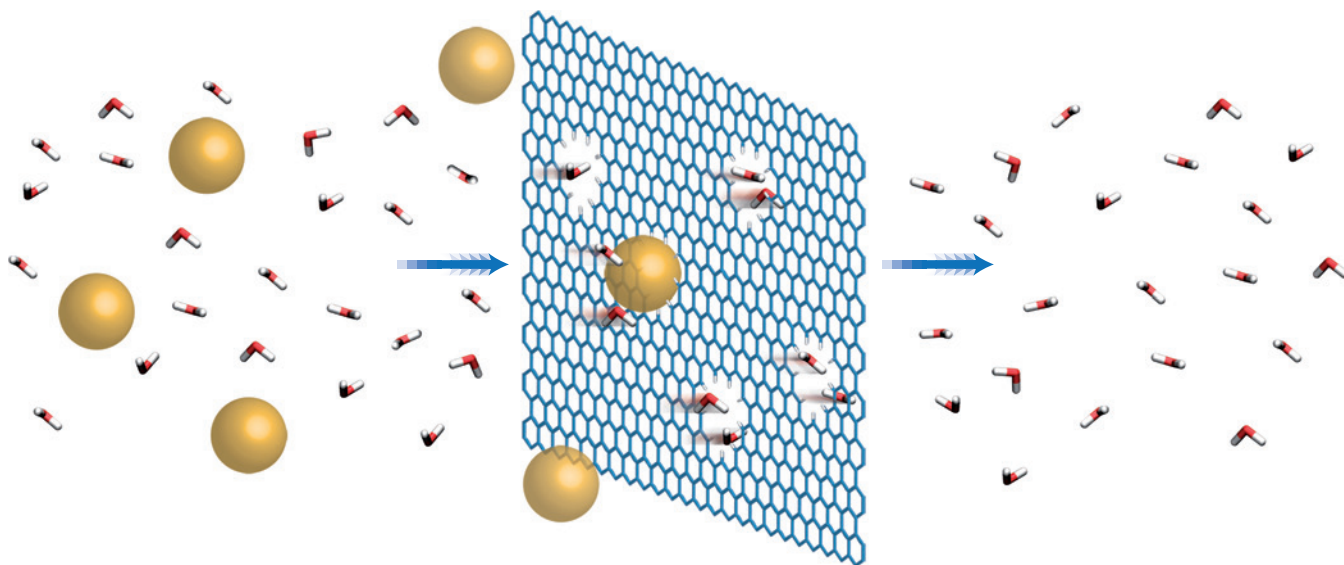


Figure 1 | A graphene membrane with subnanometre pores is a promising reverse osmosis membrane. High pressure applied to the salt water (left) drives water molecules (red and white) across the graphene membrane (right), while salt ions (spheres) are blocked. Chemical functionalization of the pores with hydrogen (white) increases water selectivity, whereas functionalization with hydroxyl groups (not shown) increases the speed of water transport.

membrane fouling and slow water transport. New membrane materials are needed to address these issues. Now, writing in *Nano Letters*, David Cohen-Tanugi and Jeffrey Grossman at the Massachusetts Institute of Technology have calculated that graphene with subnanometre pores can surpass the water permeability of current polymeric reverse osmosis membranes by two to three orders of magnitude, making it a high-performance membrane for water desalination².

State-of-the-art polymeric reverse osmosis membranes rely on the solution-diffusion mechanism, in which water molecules are selectively absorbed into a thin layer at the surface of the membrane and then diffuse across to the other side. Polymeric membranes offer excellent salt rejection, but the diffusive transport of water through the disordered polymer is slow. Recent research has therefore focused on increasing water throughput by molecular sieving in nanostructured membranes with rigid, well-defined size-selective pores such as carbon nanotubes³ or zeolites⁴. These membranes, however, are difficult to manufacture in a scalable and low-cost fashion, and have thus far demonstrated limited performance. In particular, the smallest carbon nanotubes used for membranes are still too large to effectively exclude salt ions, while the fabrication of thin, continuous zeolite layers is exceptionally challenging.

Cohen-Tanugi and Grossman show that graphene — with its high mechanical strength, atomic thickness and ability to

support subnanometre pores — has the potential to overcome these issues. Building on studies of transport of gases and ions through pores in graphene membranes^{5,6}, Cohen-Tanugi and Grossman show that nanoporous graphene membranes can successfully desalinate water (Fig. 1). They use molecular dynamics simulations to predict that nanoporous graphene membranes can provide water transport of up to 66 L per cm²·day·MPa, with >99% salt rejection. By comparison, a typical reverse osmosis membrane provides water transport of ~0.01–0.05 L per cm²·day·MPa, with comparable rejection⁷. They attribute the fast flow rate of water to the atomic thickness of the graphene membrane.

The researchers also provide insights into the mechanisms of water transport. They show that graphene pores chemically functionalized with hydrogen are better at rejecting salt ions, but have lower flow rates than pores functionalized with hydroxyl groups. This is because the water molecules need to have a particular orientation before they are able to pass through a hydrogenated pore, causing an entropic penalty that decreases the flow rate. Interestingly, the researchers find that hydroxyl groups can substitute for water in the hydration shell of salt ions, and therefore permit some ions to flow, reducing the salt rejection ratio. They also show that the graphene membranes lose their ability to reject salt as pressure increases. This is the result of the molecular volume of salt ions, which is greater than that of water molecules and causes the salt ions to be more affected by

pressure increases than water molecules. Based on their simulations, Cohen-Tanugi and Grossman identify the ideal sizes for hydrogenated pores (23.1 Å²) and hydroxylated pores (16.3 Å²) to maximize water throughput.

Although these results are promising, much work remains to demonstrate the practicality of these membranes. To place this challenge into context, reverse osmosis was first proposed for water desalination in the early 1950s, but required nearly two decades of development and major advances in materials and fabrication before it could be commercialized. However, there are indications that graphene membranes may be different. The extraordinary properties of graphene are driving research and development at an unprecedented pace. Large areas of graphene can already be grown on plain copper foils at atmospheric pressure, and roll-to-roll transfer of 30-inch graphene sheets has been demonstrated⁸. More significantly, graphene pores in the size range suggested by Cohen-Tanugi and Grossman were recently realized using ion and electron bombardment⁹, even though more work is needed to achieve monodisperse pore sizes and the desired chemical functionalization.

Perhaps the greatest difficulty will be the scalable manufacturing of large graphene membranes with subnanometre pores with a narrow size distribution, while maintaining the structural integrity of the graphene and keeping costs low. Graphene membranes will also need to be robust over time, and avoid excessive fouling under operating conditions. Furthermore, membrane

modules must be designed to rapidly remove the salt that concentrates on the feed side at high flow rates¹⁰. Although the solution to these practical issues is not clear at the moment, graphene membranes will certainly offer novel and tunable transport properties. These issues present the research community with a challenge and an opportunity that could very well make clean water more accessible around the globe. □

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NANOPATTERNING

The chemical way to ion irradiation

Local proton irradiation causes a chemical reaction that leads to nanopatterned magnetic media. The technique has strong potential for improving high-density data storage and other types of applications involving nanostructuring of materials.

Jürgen Fassbender

The applications of ion beams span a broad range, from surface finishing of materials (for example, exhaust turbochargers, machine tools, medical implants), the creation of functional layers in solar cells (for example, efficient absorbers, transparent electrodes) to electronic components for micro-, opto- and high-power electronics (for example, transistors, semiconductor detectors, light-emitting diodes, high-power switches). In the case of ion implantation, the ions are incorporated into the material and act as dopants. In the case of ion irradiation, the associated creation of disorder or vacancies (which, for example, leads to a faster electron–hole recombination in semiconductors) is the primary origin of thin-film functionalization and optimization of electronic device performances. Now writing in *Nature Nanotechnology*, Sanghoon Kim and colleagues¹ at the Yonsei University, Seoul, Korea report that ion irradiation can modify a material locally by causing chemical reactions.

The disorder created by ion irradiation in crystalline films can be extreme. In semiconductors, for example, it can lead to amorphization, which is a major drawback of doping by ion implantation. In this case, an additional annealing step is required to recover the previous crystalline structure. Metals are instead typically insensitive to ion irradiation, except for special binary alloys that favour a chemically ordered phase in thermodynamic equilibrium, like $L1_0$ -FePt or B2-FeAl (Fig. 1), and for which the situation is quite complex. The ion-irradiation-induced disorder in these alloys can lead to a modification of their magnetic properties. In

some special cases however, ion irradiation can actually create local order, because the energy provided by the ions produces local annealing.

A common strategy used to maximize the ion irradiation effect is to use multilayer structures. These consist of alternating layers of different materials, each only a few atomic layers thick. This way, the number of interfaces for a given material thickness is increased and ion irradiation causes intermixing across them, and can dramatically alter all kinds of material properties that rely on atomically sharp interfaces.

Ion irradiation in multilayer structures was demonstrated, for example, in magnetic multilayers synthesized by Chappert and co-workers². They showed that it was possible to fabricate lateral patterns of areas with different magnetic properties without introducing any topographic features. This was achieved by taking advantage of the very small interaction volume of irradiated ions with their solid-state target³. The demonstration was an important achievement showing the potential of ion irradiation for patterned media applications for high-density data storage. Unfortunately however, the requirements for such applications are very stringent. The ferromagnetic features have to be only a few nanometres across, be embedded in a paramagnetic matrix and must possess strong perpendicular magnetic anisotropy. The use of ion irradiation to modify the ferromagnetic local order and disorder properties is insufficient to satisfy all these demands. In

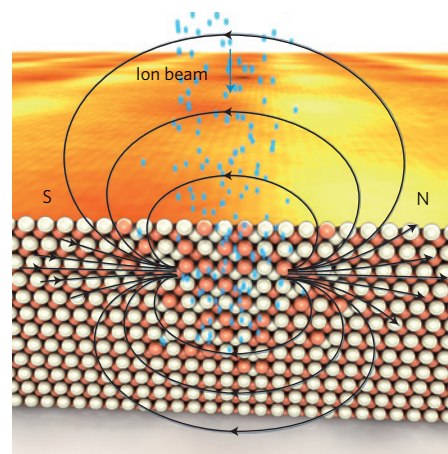


Figure 1 | Schematic of ion-induced disorder of a binary alloy. The white (Al) and red (Fe) balls indicate the different atomic species in the FeAl alloy. In the chemically ordered B2-phase all atoms are located regularly at predefined positions. Owing to ion irradiation (blue), a transformation to the chemically disordered A1-phase is achieved, where each lattice site is occupied randomly by either Fe or Al (centre of image). The change in chemical ordering is accompanied by a transition from paramagnetic (chemically ordered) to ferromagnetic (chemically disordered). A magnetic force microscopy image of the surface acquired in an applied magnetic field is superposed showing the magnetic stray fields arising from the magnetic nanostructure. The yellow regions show where the stray field is coming out of the surface, and the orange regions where it enters the surface. Image courtesy of HZDR/Sander Muenster.

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